METAL PHOSPHONATE MONOLAYERS: DEVELOPMENT OF A
PHOSPHORYLATED TEMPLATE USING ORGANIC
SELF ASSEMBLY

By

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ACKNOWLEDGEMENTS

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Abstract of Thesis Presented to the Graduate School
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Layered inorganic solids have been used as models for the study of two

dimensional magnetism. In the study of these quasi-two dimensional systems, it is

assumed that the intralayer interactions are insignificant relative to the interactions

between metal centers within a single layer. If a single layer of one of these layered

solids could be isolated for the study of low dimensional magnetism, the need to make

such an assumption could be eliminated.

The research presented in this thesis covers the progress which has been made

toward the preparation of a magnetic monolayer based on layered metal phosphonates.

The results include the study of the magnetic behavior of the layered solid manganese

phenylphosphonate, $Mn(O_3PC_6H_5)H_2O$, and the preparation of a phosphonic acid

terminated organic self assembly monolayer which can be used as a template for the construction of inorganic monolayers.

INTRODUCTION

Objective

The goal of this research is to synthesize a monolayer analog of a layered inorganic solid for the study of magnetism in two dimensions. The question of whether or not a truly two-dimensional system can undergo a transition to long range magnetic order is a fundamental one[1]. Layered inorganic-organic solids, which have the general structure shown in Figure 1, have been used as models for the study of two-dimensional magnetism. In the study of these quasi two-dimensional solids, it is assumed that the intralayer interactions are insignificant relative to the interactions between metal centers within a single layer. The need to make such an assumption could be eliminated by studying a true inorganic monolayer.

Our approach to the synthesis of a magnetic monolayer is to utilize an appropriately functionalized organic template to bind the metal centers of interest. Transition metal ions and complexes have been bound at the functionalized surfaces of oriented organic monolayers prepared by either the Langmuir-Blodgett technique or the Self Assembly technique[2,3]. By using an inorganic system which naturally forms a layered inorganic-organic solid, it may be possible to construct an inorganic monolayer in which the metal ions are not only bound to the organic template, but are also bound to each other in a manner analogous to the interaction found in the lattice of the bulk

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ORGANIC LAYER
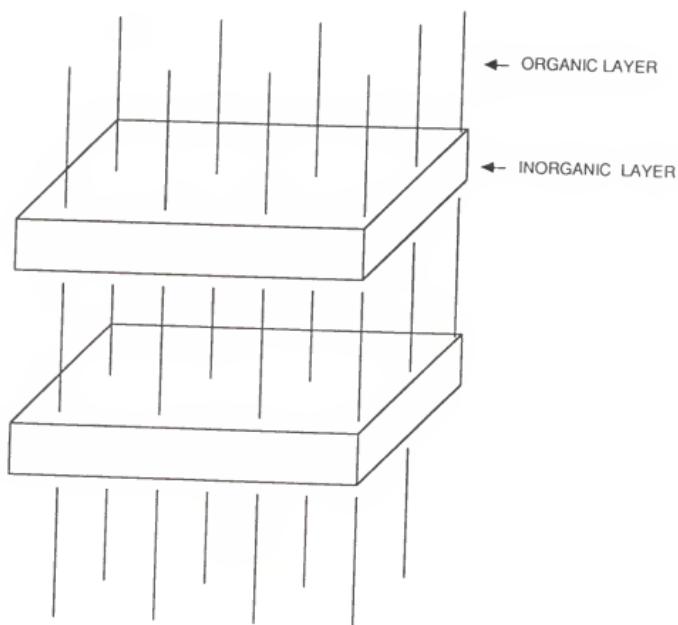
INORGANIC LAYER

Figure 1   Structure of a layered organic-inorganic solid

solid. Figure 2 depicts the synthesis of such an inorganic monolayer at an organic template.

Taking advantage of the fact that zirconium forms a layered solid with organophosphonic acids, Mallouk has synthesized a zirconium phosphonate monolayer with a structure which is apparently analogous to that of the bulk solid[4]. This inorganic monolayer was formed at a self assembled organic template. Although the tetravalent zirconium in this example is not interesting for the study of magnetic ordering, a number of paramagnetic transition metal ions, such as divalent Mn and Cu, also form layered phosphonate structures in the bulk[5,6]. Thus, it may be possible to synthesize a magnetic monolayer based on one or more of these other metal phosphonates.

The research presented in this thesis covers the progress which has been made toward the preparation of a magnetic monolayer based on layered metal phosphonates. The results include the study of the magnetic behavior of the bulk layered solid manganese phenylphosphonate, $Mn(O_3PC_6H_5)H_2O$, and the preparation of a phosphonic acid terminated organic self assembly monolayer which can be used as a template for the construction of inorganic monolayers.

Background: SA Monolayers

The formation of close-packed, highly organized mono- and multilayer films by spontaneous molecular self assembly has recently been the subject of much research in
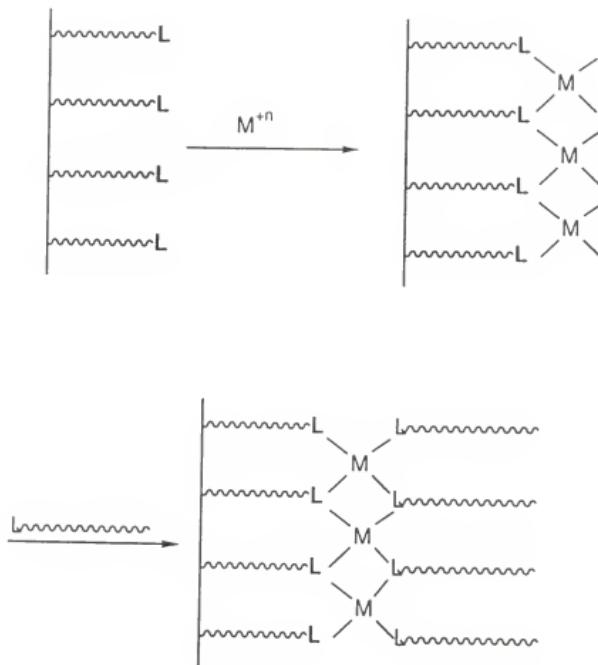
Figure 2   Synthesis of an inorganic monolayer at an organic template

chemistry and materials science. The self assembly technique allows the formation of thin films with precise control over parameters such as film thickness, molecular orientation, and the functionality present within the film[2,7,8]. These films have a variety of realized and potential applications in areas including molecular electronics[7], nonlinear optics[7,9-12], chemical sensing[13,14], immobilization of biomolecules[15,16], adhesive and protective coatings[17-19], and electrochemistry[20,21].

Long alkyl chain molecules with a surface active "headgroup" are known to spontaneously assemble from solution into monolayer films on an appropriate substrate immersed in the solution. This phenomenon, pictured schematically in Figure 3, was first reported in the literature by Zisman and coworkers[22] in the 1940's, but it was not until more recently that such films were extensively studied. The chemical binding of the headgroup to the substrate, plus the Van der Waals interactions between the long organic chains extending away from the surface, leads to the desired stability and orientation in these monolayer assemblies[2,7]. Most of the work to date has been done on monolayers of organotrichlorosilanes on hydroxylated surfaces such as SiO_2 and monolayers of alkyl thiols and disulfides on gold.

Sagiv, who performed much of the early work on the development and characterization of self-assembled (SA) monolayers, showed that functionalized long alkyl chains could be used for the formation of monolayers which are similar in organization and structure to Langmuir-Blodgett (LB) monolayers[23-27]. LB monolayers are formed by first spreading amphiphilic molecules at an air-water interface, and then compressing these molecules into a close-packed monolayer with a movable barrier.

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molecules in solution

surface active group

self assembled monolayer
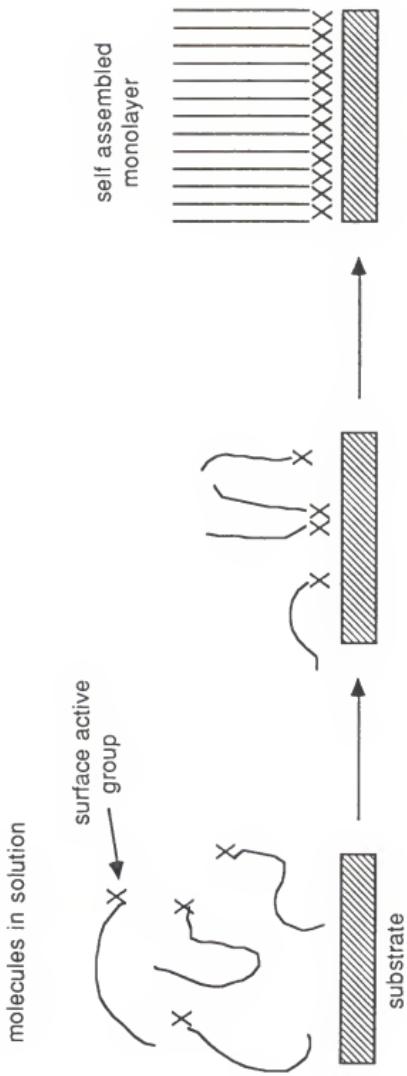
substrate

Figure 3   Formation of Self Assembled monolayers

The compressed monolayer can then be transferred to a solid support by dipping the support through the monolayer film[3]. Since SA monolayers are chemically bound to the substrate, they are more stable than their LB counterparts.

Monolayer films prepared in this research were formed by the assembly of trichlorosilanes onto SiO_2 surfaces. The mechanism for adsorption involves hydrolysis of the reactive chloro groups attached to the silicon, followed by condensation of the resulting silanols with each other and the hydroxylated surface. Surfaces have been derivatized with organosilanes for years; examples include the derivatization of chromatographic supports and the use of silanes as coupling agents[17,28]. However, for uses such as these, a thin polysiloxane film is usually formed on the surface, instead of a single monolayer. In monolayer formation, adsorption is done from hydrocarbon solvents where only a trace amount of water is present. Usually, enough water is present on the hydrophilic silica surface to promote the hydrolysis and subsequent condensation of a single monolayer of the silane[7]. Using long alkyl chain silanes also promotes the formation of a monolayer film, because the long organic backbone extending away from the surface blocks the adsorbed silane headgroup from further condensation with silanes in solution.

Since the initial work by Sagiv on monolayers of octadecyltrichlorosilane[23], a variety of more interesting functional groups have been incorporated into SA films. Functional groups have been incorporated at terminal and internal positions. When the alkyl chain is terminally functionalized, a surface containing a dense array of that functional group results after SA monolayer formation. Examples of terminal

functional groups which have been incorporated into SA films include alkene[26], alcohol[26,29], ester[29], and bromide, nitrile, amine and thiocyanate[30]. In addition, chemical reactions can be performed on the monolayer assembly to convert one functional group into another without destroying the film. An example is the work of Sukenik and Balachander which demonstrates the conversion of a bromide terminated monolayer to a nitrile terminated monolayer, followed by reduction of the nitrile to an amine[30]. Functionality has also been incorporated into the organic backbone of self assembling molecules. This internal functionalization can be as simple as the insertion of a phenoxy[31] or sulfone[32,33] group into the long alkyl chain typically used for monolayer formation, or as complex as assembling large conjugated dye molecules functionalized with surface active headgroups in place of the more common alkyl chain backbone[11,12].

Multilayer assemblies can also be constructed, one layer at a time, by self-assembly. Early procedures for multilayer construction involved the initial adsorption of an organotrichlorosilane with a terminal functional group which could then be activated toward the assembly of a second layer[26,29]. An example is the work of Sagiv in which a silane with a terminal alkene is assembled into a monolayer. The alkene is then activated by a hydroboration reaction to give an alcohol terminated monolayer[26]. A second silane can then be adsorbed onto this hydroxylated surface. This approach to multilayers has proved not useful for very thick films, as defects usually become significant after deposition of only a few layers.

More recently, Mallouk has reported another technique for assembling multilayers which is perhaps superior to that described above[4]. Mallouk's technique takes advantage of the fact that tetravalent zirconium forms highly insoluble layered solids with organophosphonic acids. Thus zirconium ions will bind to a phosphorylated surface from aqueous solution. Multilayers can then be built up one layer at a time by the alternate adsorption of bisphosphonic acids and more zirconium ions, as is depicted in Figure 4. The structure of the multilayer film obtained by this procedure is thought to be analogous to that of the bulk layered zirconium organophosphonate. Because of the strong zirconium phosphonate linkages which not only bind the layers together, but also bridge the organic molecules within a single layer, these multilayer assemblies are particularly robust.

A variation of Mallouk's technique for the formation of multilayers with zirconium phosphonate linkages has been used by Chidsey and coworkers to assemble stable multilayer organic films containing polar molecules with all of the dipoles aligned in the same direction[11,12]. After the initial phosphorylation and zirconation of the surface, an organic dye molecule with a phosphonic acid group on one end and an OH or NH_2 group on the other end is adsorbed. Because only the phosphonic acid end of the molecule attaches to the zirconated surface, all of the dye molecules are oriented in the same direction. After the assembly of this oriented polar layer, the resulting surface of alcohol or amine groups is phosphorylated with $POCl_3$. Additional layers can be built up by repeating the adsorption and conversion sequence.
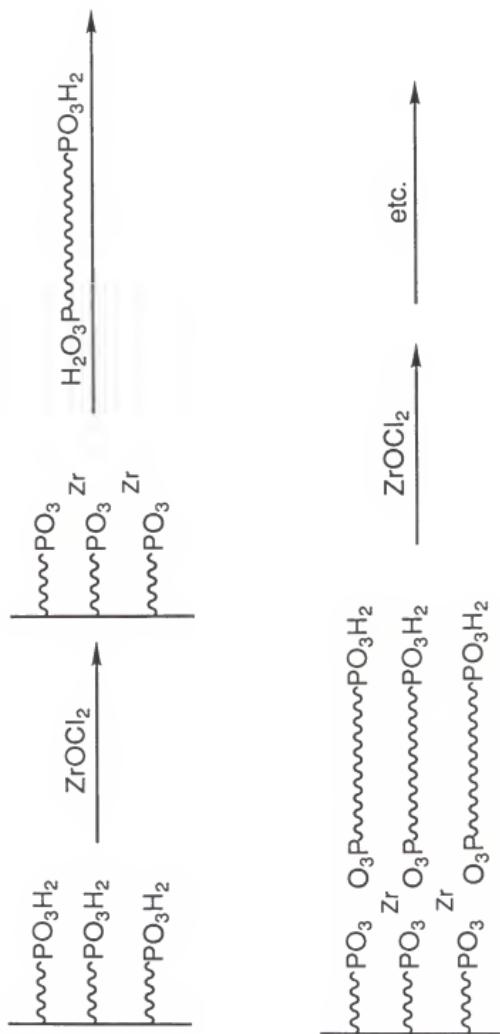
Figure 4   Mallouk's technique for the synthesis of zirconium phosphonate multilayers

A number of techniques have been applied to the characterization of SA mono- and multilayer films. These techniques have been reviewed by Ulman[2]. The most widely used techniques include contact angle measurements, ellipsometry, x-ray photoelectron spectroscopy, and Fourier Transform Infrared Spectroscopy.

Contact angle is a measure of the degree of spreading of a liquid on a surface[34]. The contact angle of a monolayer coated surface with a liquid depends on the functional groups present in the film, as well as the degree of coverage. For example, water beads on a hydrophobic octadecyltrichlorosilane monolayer, giving a contact angle of 112 degrees[23]. An amine terminated monolayer has a much lower water contact angle of 63 degrees[30]. This lower contact angle is expected because water should have more of an affinity for the amine surface. In a more quantitative application, contact angle measurements can be used to calculate the surface free energy or critical surface tension. A Zisman plot is obtained by measuring contact angles of a series of liquids with known surface tensions, then plotting cosine of the contact angle vs. liquid surface tension. When this linear plot is extrapolated to the point where the contact angle equals zero, the surface tension of the solid can be read off of the liquid surface tension axis[34].

Ellipsometry is a technique for calculating the thickness of a thin film on a reflecting surface[35]. In ellipsometry, a polarized beam of monochromatic light is reflected at an angle off of a surface. A thin film coated on the surface can cause a change in the polarization of the light when the beam travels through the film. If the refractive index of the film is known or can be estimated, the measured change in

polarization can be used to calculate the thickness of the film. This technique has been used to measure the thickness of individual monolayers, and has been used to monitor the increase in thickness which occurs after each step in a multilayer deposition[4,24,36].

Electron Spectroscopy for Chemical Analysis (ESCA), also known as X-Ray Photoelectron Spectroscopy (XPS), can be used to determine what elements are present in a SA film, and can also provide an estimate of the relative amounts of those elements[37]. In ESCA, x-radiation of a constant frequency is directed onto a sample, causing the ionization of core electrons. Energy from the incident x-rays not used for ionization is imparted to the escaping electrons in the form of kinetic energy. Thus, electrons from different elements, which have different binding energies, will escape with different amounts of kinetic energy. The detector measures this kinetic energy, and since the frequency of the ionizing x-ray is known, the measured kinetic energy is used to calculate the binding energy of the escaping electron. The binding energy can then be correlated to an element which must be present on the sample surface. Integration of peak areas for various binding energies gives an indication of the relative amounts of each element present. Sukenik has used ESCA to confirm the presence of functional groups in SA monolayers, and to monitor the conversion of one functional group into another[30]. Angular-dependent ESCA, a technique which determines the elements present at various depths into the sample by varying the angle at which the ejected electrons are detected, has been used to profile a trilayer film in which each layer contains a different metal ion[38].

Two different types of Fourier Transform Infrared Spectroscopy can be used to obtain spectra of mono- and multilayer films. Reflection-Absorption Infrared Spectroscopy (RAIRS), also called External Reflectance Infrared Spectroscopy (ER-IRS), is useful for obtaining spectra of films on highly reflective substrates, and has thus been applied to the study of monolayers on substrates such as gold and aluminum mirrors[24,36]. RAIRS employs an infrared beam polarized parallel to the plane of incidence (p-polarized) which is impinged upon the reflecting surface at a grazing angle. This combination of p-polarization and grazing angle incidence creates a standing wave of the electric field component aligned normal to the surface which gives an enhanced signal relative to that which would be obtained by simple transmission of an IR beam through the monolayer film[39,40]. Because the electric field is oriented perpendicular to the surface, this technique is sensitive to the orientation of the monolayer film[24,40]. For example, in a monolayer spectrum of long alkyl chain molecules on an aluminum mirror, the methyl signals are much larger than what might be expected, and the methylene bands are relatively weak. These band intensities are evidence that the alkyl chains are oriented approximately perpendicular to the surface. In this orientation, the methyl group has a vibrational mode aligned along the electric field, and thus has an increased signal. The methylene vibrations, however, are parallel to the surface or perpendicular to the electric field, so they do not have an enhanced signal.

A second infrared technique which can be used for sampling monolayer films is Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR).

ATR-FTIR utilizes the principle of total internal reflection[39]. In this technique, the infrared beam enters the face of a specially cut optical crystal and is propagated through the length of the crystal by reflection between the two long edges of the crystal, as is shown in Figure 5. If a monolayer film is coated on the outside of this crystal, the absorption spectrum is measured each time the light beam contacts the interface, giving an attenuated infrared spectrum of the film. ATR-FTIR spectra are generally more intense than spectra obtained from RAIRS because of multiple sampling of the film. ATR-FTIR is not as sensitive to film orientation as is RAIRS, however, some information on orientation can be obtained from this technique. Sagiv[23] has measured ATR spectra of a number of monolayer films using both s- and p-polarized radiation, and then compared the measured dichroic ratios (ratio of absorbances of a particular IR band in the parallel and perpendicular spectra) to those calculated from theoretical models for different possible orientations. This technique can only be used as an approximate gauge of orientation since many factors which are difficult to control can cause significant changes in the measured dichroic ratios.

Extensive research has been done in recent years on monolayer films formed by spontaneous molecular self assembly from solution. This research has shown that film properties can be tailored by the incorporation of functional groups, and that organized multilayer assemblies can be constructed by sequential deposition of monolayers. Also, it has been demonstrated that a large number of analytical techniques can be applied to the characterization of these ultrathin films.

to detector

mirror

mirror

ATR crystal

from source
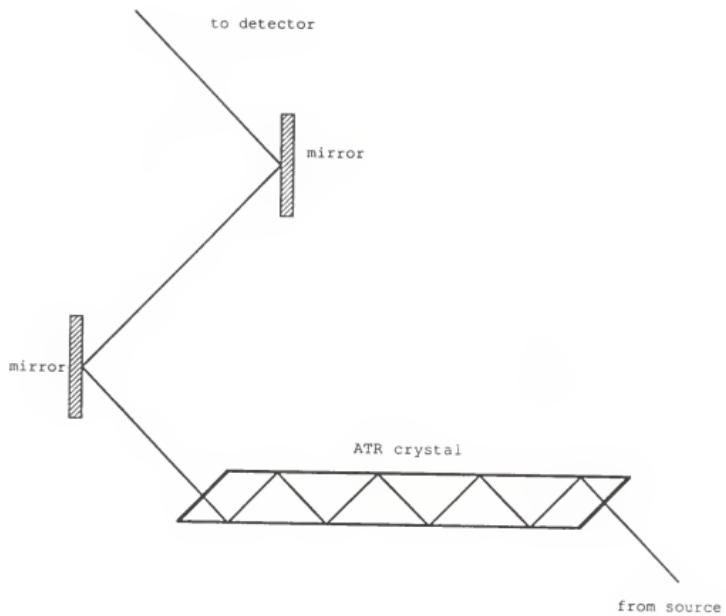
Figure 5   Diagram of the optical path for ATR-FTIR

EXPERIMENTAL

General

Octadecyltrichlorosilane, ω-undecenyl alcohol, chloroplatinic acid, trichlorosilane, triethylphosphite, octadecylbromide, 1,10-dichlorodecane, phenylphosphonic acid, and zirconyl chloride were purchased from Aldrich and used as received. Manganese chloride, 1,5-dibromopentane, and lithium bromide were purchased from Fisher and used as received. Triethoxysilane was purchased from Alfa, and bicyclohexyl was purchased from TCI America.

Tetrahydrofuran was dried over Na and distilled. Acetonitrile and triethylamine were distilled from CaH_2. Methylene chloride was distilled from P_2O_5. Methane sulfonyl chloride was distilled. Chloroform was spectra grade and was used as received. All of these reagents were purchased from Fisher. All other reagents were purchased from commercial sources and used without further purification.

Silicon wafers (n-type) were purchased from Semiconductor Processing Co.. Si ATR crystals, 50x10x3mm parallelograms, were purchased from Wilmad Glass Co.. Water was obtained from a Barnstead Nanopure system.

FTIR spectra were recorded on a Mattson Research Series 1 instrument using a liquid nitrogen cooled MCT detector. A Harrick TPM stage was used for the ATR experiment. Single beam spectra of 1000-5000 scans at 4 cm^{-1} resolution were

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recorded for monolayers coated on ATR crystals. These single beam spectra were ratioed to a background spectrum recorded using the uncoated crystal.

ESCA analyses were performed on a Perkin Elmer PHI5000 Series spectrometer using a Mg Kα source (1253.6eV). The instrument is equipped with a variable angle stage and a hemispherical energy analyzer and operates at a base pressure of 10^{-8}-10^{-9} torr.

Compound Syntheses

ω-Undecenylbromide. This compound was synthesized from commercially available ω-undecenyl alcohol by the procedure of Sukenik and Balachander[30]. Proton NMR and IR spectra are in agreement with those reported by Sukenik and Balachander.

ω-Hexadecenylbromide. The procedure of Sukenik and Balachander[30] was also used for the synthesis of this compound, but with the following modification: The Grignard reaction was done on a much larger scale so that the product could be purified by fractional distillation, instead of on an HPLC column. For Grignard formation, 60.5g (0.26mol) of ω-undecenylbromide was placed into the addition funnel and 16g (0.65mol) of Mg turnings were placed in a 500ml round bottom flask. After formation, the Grignard reagent was transferred by cannula to a 1l flask containing 106ml (0.78mol) of 1,5-dibromopentane and 15ml of 0.2M CuCl$_2$ and LiCl in THF, all dissolved in 600ml THF. After reaction, the excess 1,5-dibromopentane was removed by vacuum distillation. The resulting oil was distilled through a fractionating column

to give the desired ω-hexadecenylbromide (110°C, 0.4 torr). The yield was 45.8g, or 58% based on moles of ω-undecenylbromide used. Proton NMR and IR spectra are in agreement with those reported by Sukenik and Balachander.

    1-Bromo-11-(trichlorosilyl)undecane and 1-bromo-16-(trichlorosilyl)hexadecane. The procedure used is similar to the hydrosilylation procedure used by Sukenik and Balachander[30] to synthesize the latter of these two compounds. Glass tubes approximately six inches in length and 1 inch in diameter with teflon rotoflo stopcocks were used as reaction vessels. In a typical procedure, 5g of either ω-undecenylbromide or ω-hexadecenylbromide were placed into the reaction tube, along with 0.5ml of a 4% solution of chloroplatinic acid in isopropanol and a magnetic stir bar. The tube was then introduced into a nitrogen glove box where 15ml of trichlorosilane was added and the tube sealed. Bubbling and evolution of heat usually occurred immediately upon addition of the silane to the alkene. The sealed tube was removed from the glove box and placed in a warm oil bath (50-70°C) for 15-20 hours. After this time, the tube was removed from the oil bath and allowed to cool to room temperature. To relieve pressure which may have built up during the reaction, the tube was vented to an Argon line. The excess trichlorosilane was removed by slowly opening the stopcock to vacuum and condensing the trichlorosilane in a dry ice-acetone trap. Because the trichlorosilane is very volatile, bumping occurs during this removal. However, if evacuation is done very slowly while stirring, there is enough room in the tube to allow for bumping without losing product by bumping it over into the cold trap. After all of the excess trichlorosilane was removed, the tube was

backfilled with Ar, and again introduced into a nitrogen glove box, where the contents of the reaction vessel were transferred to a short path distillation apparatus. The product was then recovered by vacuum distillation. Proton NMR and IR are in agreement with those reported by Sukenik and Balachander.

Trichlorosilane, which is very volatile and corrosive, was found to eat rubber septa and also destroyed a teflon lined septum after only one puncture was made in the teflon. Simply opening a large bottle of $HSiCl_3$ and pouring out the desired volume filled the glove box with vapors which corroded the inside of the box and escaped into the lab when removing items from the box via the antechamber. Thus the following technique was employed for the transfer of $HSiCl_3$ to the reaction tubes. The trichlorosilane was transferred from the bottle in which it was purchased to a 500ml round bottom flask with a teflon stopcock sidearm attached near the top. This flask is stored in a nitrogen filled glove box. A syringe fitted with a 12 inch teflon needle and a locking hub was used to transfer the trichlorosilane. To transfer $HSiCl_3$, the stopcock of the storage flask is opened and the teflon needle inserted into the flask through the stopcock opening. When the appropriate volume of silane has been drawn into the syringe, the hub is locked, the needle withdrawn, and the stopcock closed. The trichlorosilane can then be added to the reaction tube by opening the rotoflo stopcock, inserting the needle, and unlocking the hub. This procedure allows for safe and easy transfer of the volatile $HSiCl_3$ without having to open a large container and thus fill the box with corrosive vapors.

Diethyl ω-undecenylphosphonate. This compound was synthesized from ω-undecenylbromide by a Michaelis-Arbuzov reaction. In a typical procedure, 20.0g (0.086mol) of the bromide and 29.0ml (0.17mol) triethylphosphite were added to a 100ml round bottom flask fitted with a reflux condenser, Ar inlet, and magnetic stir bar. The reaction mixture was heated to reflux under Ar for 24 hours, and then the excess triethylphosphite was removed by distillation. The pure product was isolated by vacuum distillation (115°C, 0.3torr). The product was identified by proton NMR and IR. The NMR spectrum contained the following peaks: 1.2-1.8ppm, multiplet, 22H; 2.0-2.1ppm, quartet, 2H; 4.0-4.2ppm, multiplet, 4H; 4.9-5.1ppm, multiplet, 2H; 5.7-5.9, multiplet, 1H. Major bands in the IR include 3082, 2986, 2928, 2854, 1645, 1462, 1249, 1165, 1060, 1028, and 960cm^{-1}.

Diethyl 11-(triethoxysilyl)undecanephosphonate. In a typical procedure, 10.0ml (0.034mol) diethyl ω-undecenylphosphonate, 15.0ml (0.1 mol) triethoxysilane, and 3ml of a 4% solution of chloroplatinic acid in isopropanol were added to 80ml dry acetonitrile in a 250ml round bottom flask fitted with a reflux condenser, Ar inlet, and magnetic stir bar. The reaction mixture was refluxed under Ar for at least one week. After completion of the reaction, the excess triethoxysilane was removed by vacuum distillation. The resulting oil contained an approximately 50-50 mixture of desired product and alkene which had not been hydrosilylated, but rather had isomerized to an internal alkene. These two products were easily separated by distillation. The desired product, diethyl 11-(triethoxysilyl)undecanephosphonate, was characterized by proton NMR and IR. The NMR spectrum contains the following peaks: 0.65ppm, multiplet,

2H; 1.2-1.8ppm, multiplet, 35H; 3.8ppm, multiplet, 6H; 4.0-4.2, multiplet, 4H. The major IR bands include 2976, 2929, 2854, 1461, 1384, 1250, 1164, 1107, 1083, 1035, and 959cm^{-1}.

Octadecylphosphonic acid. This acid was synthesized from commercial octadecylbromide by a Michaelis-Arbuzov reaction, followed by acid hydrolysis. In a typical procedure, 10g (0.03 mol) octadecylbromide and 10ml (0.06 mol) triethylphosphite were refluxed under Ar for 18 hours. The excess triethylphosphite was removed by distillation, and 60ml of concentrated aqueous HCl added to the flask. The acid solution was refluxed under Ar for 10 hours and then allowed to cool to room temperature. Upon cooling the solid phosphonic acid precipitated from solution. The solution was filtered and the phosphonic acid rinsed with water and then acetonitrile. The acid was recrystallized from methanol and dried under vacuum. The yield was 5g or 50%. The acid was characterized by elemental analysis and IR. %C calc. 64.7, found 65.5; %H calc. 11.7, found 12.1. The major IR bands include 2957, 2918, 2850, 1471, 1406, 1228, 1082, 1001, and 947cm^{-1}.

1,10-Decylbisphosphonic acid. The procedure which was used for the synthesis of octadecylphosphonic acid was also used for the synthesis of 1,10-decylbisphosphonic acid from commercial 1,10-dichlorodecane. However, the decylbisphosphonic acid did not immediately precipitate out of the aqueous solution upon cooling, so the solution was heated until most of the water had evaporated. Upon cooling, the acid did precipitate out of this more concentrated solution.

Manganese phenylphosphonate. This solid was synthesized using a procedure reported by Mallouk[4]. The powder was characterized by elemental analysis, IR, and powder x-ray diffraction. The results of these analyses are in agreement with those reported in the literature.

Monolayer Formation and Conversion

Substrates used for formation of SA monolayers were Si wafer pieces or a Si ATR crystal. Substrates were cleaned using the RCA cleaning procedure[41]. This cleaning procedure involves first soaking the Si substrate in a mixture of five parts warm water (70-80°C) to one part 30% H_2O_2 and one part NH_4OH for 10 minutes, followed by soaking in a mixture of 6 parts warm water to one part 30% H_2O_2 and one part concentrated HCl for 10 minutes. The substrates were rinsed thoroughly with water after each step. After cleaning, the substrates were dried in a stream of N_2 and used immediately. Monolayer coated ATR crystals were cleaned with Ar plasma in a Harrick plasma cleaner for 15-30 minutes to remove adsorbed monolayers so that they could be reused.

Alkyltrichlorosilane monolayers were formed by dipping the cleaned substrate into a bicyclohexyl (BCH) solution containing 100 microliters of silane for every 10ml of BCH. Prior to addition of the silane to the BCH, the solvent was shaken with a few drops of water, allowed to settle overnight, and then decanted. Silane solutions were prepared and used in a N_2 glove bag. Substrates remained in the silane solution for 15 minutes to an hour. Once substrates were removed from the solution, they

were rinsed with a few milliliters of $CHCl_3$ and then washed with hot $CHCl_3$ in a soxhlet extractor for 30 minutes. Used BCH was collected and distilled for reuse. Monolayers of diethyl 11-(triethoxysilyl)undecanephosphonate were also deposited from BCH solutions prepared as described above, however, the solution containing the substrate was gently heated (50-70°C). The substrate remained in this warm solution for several days to a week.

For the chemical conversion of the SA monolayers with triethylphosphite and HCl, a wide, shallow, flat-bottomed vessel with a ground glass jointed top and a matching wide mouth condenser was employed. This design allowed the fragile ATR crystals to be gently placed into and removed from the reaction vessel using teflon forceps. Once placed inside the reaction vessel, the substrate was covered with the appropriate reagent, either triethylphosphite or HCl, and the reflux condenser fitted into place. Typically, the solution was heated to reflux under Ar for 12-18 hours. Substrates removed from the triethylphosphite were rinsed with a few milliliters of $CHCl_3$ and then cleaned with hot $CHCl_3$ in a soxhlet extractor. Monolayers removed from the HCl solution were rinsed extensively with water and then dried under flowing nitrogen.

Binding of zirconium was accomplished by placing the phosphorylated substrate into a 5mM aqueous solution of $ZrOCl_2$ for 10 hours at room temperature. The substrate was washed extensively with water and dried in a stream of N_2 after removal from the Zr solution. Assembly of the capping acid, $C_{18}H_{37}PO_3H_2$, took place from a solution prepared by first dissolving enough acid in hot ethanol to give a 5mM

solution, and then adding 2ml water to every 50ml of the ethanolic solution.

Substrates were left in this solution for 12-18 hours, then removed and washed with

CHCl$_3$ as has been described previously.

RESULTS AND DISCUSSION

Bulk Manganese Phosphonates

Before attempting to synthesize a two dimensional analog of a layered inorganic lattice for the study of low dimensional magnetism, a bulk layered solid must be chosen as a model compound. This model compound should undergo a transition to long range magnetic order, so that the two dimensional magnetic behavior can be compared to this bulk transition. Since Mallouk has demonstrated the layer-by-layer synthesis of zirconium phosphonates[4], and other transition metal ions (ie. Mn^{+2}, Cu^{+2}, Fe^{+2}) are also known to form layered solids with phosphonic acids[5,6], it may be possible to use a self assembly technique similar to Mallouk's to synthesize inorganic monolayer analogs of some of these paramagnetic transition metal phosphonates. However, there are no reports in the literature indicating whether or not any of these paramagnetic transition metal phosphonates undergo a transition to long range magnetic order, thus making them a suitable model compound.

The layered solid manganese phenylphosphonate, $Mn(O_3PC_6H_5)H_2O$, was studied to determine its suitability as a bulk model. This compound was chosen for the study of the bulk magnetic properties for several reasons. Cunningham[5] reported the probability of antiferromagnetic interaction in manganese phenylphosphonate based on the difference in magnetic moment found in this material at 293 and 93K. Also,

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manganese phenylphosphonate is one of the few metal phosphonates which has been characterized in the literature by single crystal x-ray diffraction[6]. In addition, the high spin d^5 configuration of the divalent manganese in this compound provides a maximum number of unpaired spins for the investigation of the magnetic behavior in a small sample, such as a monolayer film.

Manganese phenylphosphonate powder was synthesized by a literature procedure[6] and the temperature dependence of the magnetic susceptibility measured. Figure 6 shows a plot of the magnetic susceptibility vs. temperature. It can be seen from the sharp drop in magnetic susceptibility at low temperature that this solid undergoes a transition to long range antiferromagnetic order upon cooling[1]. Mallouk has shown that changing the alkyl group in a series of manganese alkylphosphonates changes the distance between the inorganic layers, but does not change the lattice within the inorganic layers[6]. Thus the antiferromagnetic ordering seen in $Mn(O_3PC_6H_5)H_2O$ is probably a general phenomenon for a class of manganese alkylphosphonates, independent of the alkyl group. In order to prove this assumption, manganese methyl and ethylphosphonates have also been prepared, but the temperature dependence of the magnetic susceptibility has not yet been measured. Since a class of manganese alkylphosphonates most likely have the same type of magnetic interaction, the phenyl compound studied will be considered an appropriate model.
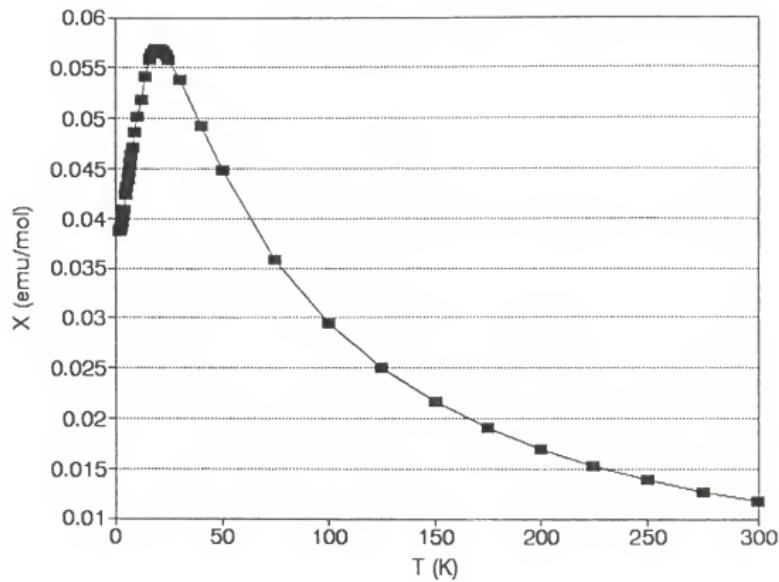
Figure 6   Temperature dependence of the magnetic susceptibility of manganese phenylphosphonate

Formation of SA Monolayers

In order to make a monolayer analog of manganese alkylphosphonates, a template consisting of an ordered two dimensional array of phosphonic acid groups is needed. The surface phosphorylation techniques used by Mallouk for the synthesis of zirconium phosphonate multilayers involve the self assembly of three or four carbon chain molecules, and thus do not take advantage of the organization which can be imparted to SA monolayers by the adsorption of long alkyl chain molecules[4,20]. The surface phosphorylation technique utilized by Chidsey requires the initial formation of a thin polysiloxane film of up to ten monolayers thickness[11]. These phosphorylation techniques may be suitable for the construction of multilayer assemblies where long chain molecules can be utilized in subsequent layers to impart order to the assembly, and the initial surface layer becomes an increasingly insignificant part of the total structure as multilayers are built up. However, if adsorption is to be halted after the formation of a single inorganic monolayer, the quality of the template used to bind the metal ions becomes very important.

Formation of a self assembled monolayer of a bifunctional long chain alkane with a trichlorosilyl group on one end and a phosphonic acid group on the other end of the carbon chain should provide the necessary ordered template of phosphonic acid groups. Figure 7 outlines the first synthetic route employed to synthesize such a template. This scheme begins with the reaction of ω-undecenylbromide with triethylphosphite to yield diethyl ω-undecenylphosphonate, followed by the chloroplatinic acid catalyzed addition of trichlorosilane across the double bond. The
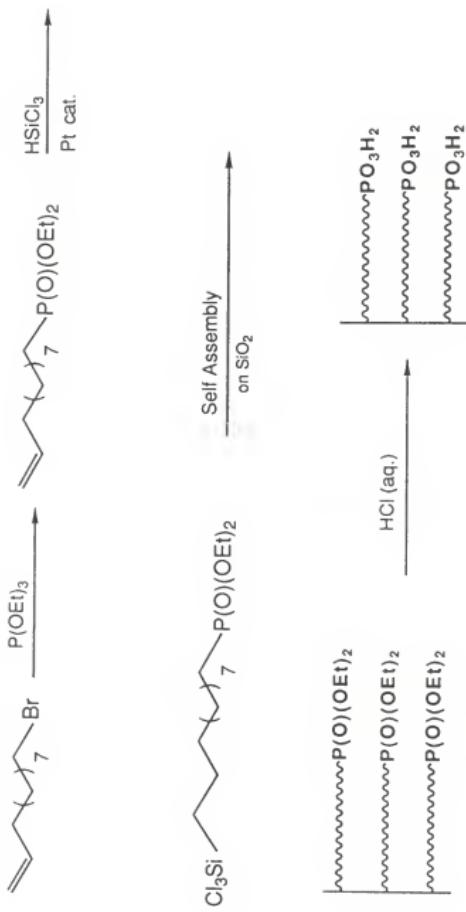
Figure 7   First synthetic scheme for a phosphorylated surface

resulting $Cl_3Si(CH_2)_{11}P(O)(OEt)_2$ is then assembled into a monolayer, and the terminal phosphonate groups hydrolyzed to the corresponding phosphonic acid.

Attempts to follow this synthetic route to a phosphorylated template were unsuccessful. Diethyl ω-undecenylphosphonate was synthesized; the proton NMR for this compound is shown in Figure 8. Repeated attempts to hydrosilylate the double bond resulted in the formation of a glassy polymer, even though extreme caution was taken to prevent moisture in the reaction. Although not very soluble in any common solvent, enough of the polymer was dissolved in $CDCl_3$ to obtain a proton NMR. Missing in this spectrum is the multiplet at 4.0ppm which is due to the methylene protons of the ethoxy groups on phosphorous. Perhaps the ethoxy groups exchanged with chlorines from the $HSiCl_3$, resulting in reactive $POCl_2$ groups. This hydrosilylation reaction was also attempted in very dry ethanol, but again the product polymerized.

Synthesis of $Cl_3Si(CH_2)_{11}P(O)(OEt)_2$ from the alkenyl bromide was also attempted by reversing the order of the hydrosilylation and Michaelis-Arbuzov reactions. Trichlorosilane was successfully added across the double bond of the bromide to give $Cl_3Si(CH_2)_{11}Br$. However, reaction of this bromide with triethylphosphite again resulted in polymer formation.

In continuing attempts to synthesize the desired phosphonic acid self assembled template, the reaction scheme outlined previously was modified by adding triethoxysilane across the double bond instead of trichlorosilane. The desired $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$ was able to be synthesized, but only with great difficulty.

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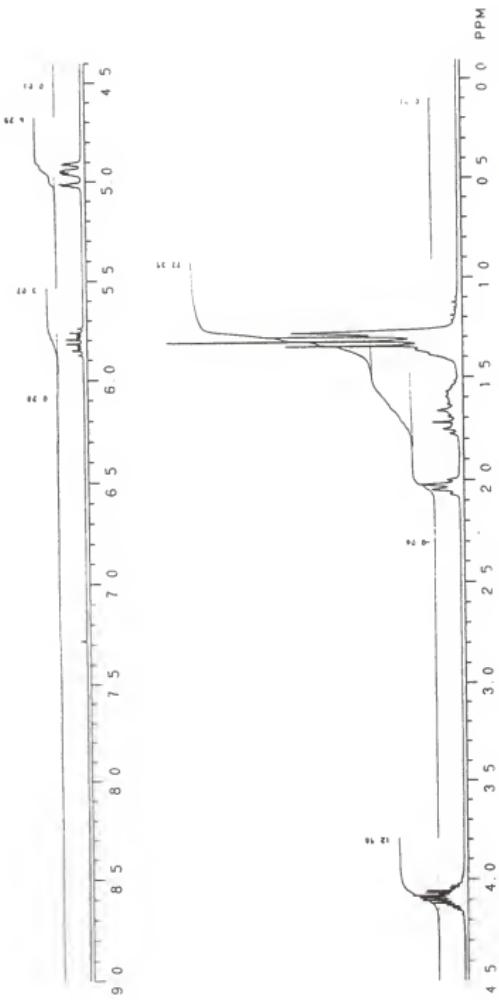
Figure 8   Proton NMR of $H_2C=CH(CH_2)_9P(O)(OEt)_2$

It appears that the phosphonate group is somehow poisoning the catalyst. The addition of triethoxysilane in the presence of chloroplatinic acid to similar alkenes terminated with bromide or nitrile groups can be accomplished in high yield by mixing the neat alkene and silane at 70°C for 10-15 hours. However, addition of triethoxysilane to the unsaturated phosphonate was only accomplished by heating the silane, alkene, and a large amount of catalyst in refluxing acetonitrile for at least one week. Approximately half of the product obtained from this reaction is the desired one. The other half of the starting alkene isomerizes to an internal position and is not hydrosilylated

In addition to the difficulty in the synthesis of diethyl (11-triethoxysilyl)undecanephosphonate, formation of self assembled monolayers of this compound is also problematic. This will be discussed later in the section on monolayer characterization.

The reaction scheme outlined in Figure 9 was the next approach attempted for the synthesis of the phosphonic acid terminated template. The ω-undecenylbromide used for the synthesis of the phosphonate in the previous scheme is first converted to ω-hexadecenylbromide by a literature preparation. This alkenylbromide is hydrosilylated with trichlorosilane and assembled into a bromide terminated monolayer. The conversion of the bromide to the phosphonate by reaction with triethylphosphite is carried out on the assembled monolayer, followed by acid hydrolysis to the phosphonic acid. All of the steps in this scheme have been successfully performed, making this a viable route to a phosphonic acid terminated template.
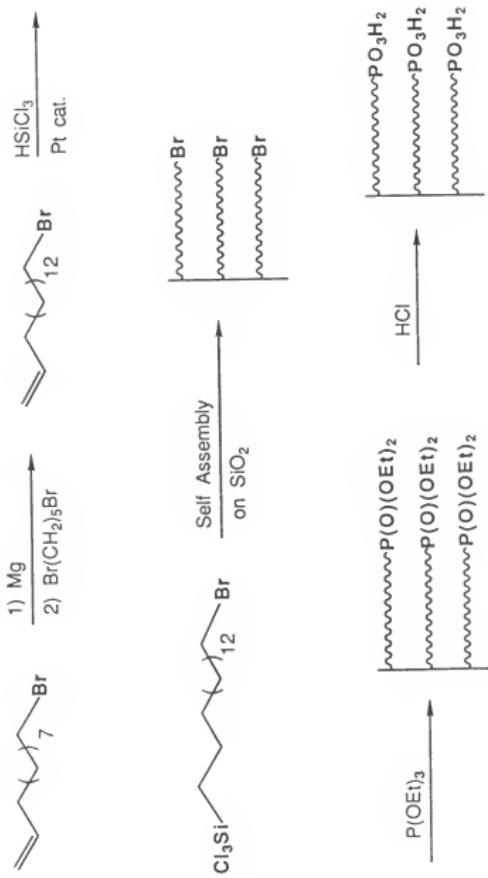
Figure 9   Second synthetic scheme for a phosphorylated surface

Although zirconium monolayers are not the inorganic monolayers of interest, this metal is known to readily bind to a phosphorylated surface. Thus, zirconium was used to determine whether or not a layered metal phosphonate could be assembled at the phosphonic acid template synthesized by this technique. The phosphorylated substrate was first immersed into an aqueous solution of $ZrOCl_2$ to bind Zr^{+4} to the phosphonic acid sites. The zirconated sample was then immersed into a solution of a "capping" acid, $C_{18}PO_3H_2$, to complete the formation the metal phosphonate monolayer, as is shown in Figure 10. As will be shown in the section on characterization, zirconium ions have in fact been incorporated at this phosphonic acid template, but the present assembly conditions do not appear to promote formation of a completely capped zirconium phosphonate monolayer.

A similar procedure has been used, without success, to attempt to bind Mn^{+2} to the phosphonic acid sites in this monolayer film. To bind manganese, the substrate was immersed into a 5mM aqueous solution of manganese chloride, however no evidence of manganese binding to the substrate could be detected. This experiment was repeated with the pH of the aqueous solution of manganese chloride adjusted to five, since bulk manganese phenylphosphonate is not soluble in water at this pH. Manganese hydroxide precipitated out of the solution after several hours, but again there is no evidence to indicate that any manganese is bound to the phosphonic acid monolayer. It is not surprising that the manganese does not bind to the phosphorylated template as readily as does the zirconium. The tetravalent zirconium binds very tightly to the phosphonate group, rendering the zirconium phosphonate
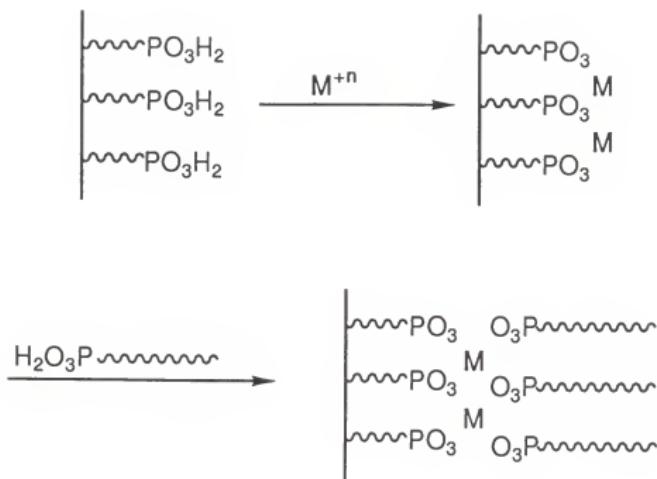
Figure 10   Binding of inorganic ions and capping layer at organic template

solids totally insoluble in water, even at low pH. However, divalent manganese phenylphosphonate is soluble in water at low pH, which indicates that the manganese does not bind to the phosphonate group quite as tightly as the zirconium.

Monolayer Characterization: ATR-FTIR and ESCA

SA monolayers of octadecyltrichlorosilane (OTS) have been extensively studied, and are thus used as standards for comparison in the characterization of other monolayer films[2,23]. Figure 11 shows an ATR-FTIR spectrum of OTS on a Si ATR crystal. Because the silicon substrate absorbs below 1500 cm^{-1}, the entire IR spectrum can not be recorded. The bands at 2918 and 2850 cm^{-1} are the asymmetric and symmetric methylene stretches, respectively, and the band at 2958 cm^{-1} is due to the asymmetric methyl stretch. The symmetric methyl stretch, which occurs at approximately 2878 cm^{-1}, is not resolved but appears as a tail on the asymmetric methylene peak. The position and width of the asymmetric methylene band at 2918 cm^{-1} have been used as indicators of the close-packing and crystalinity of SA monolayers[23,33,42]. In the OTS spectrum shown, the position of this band at 2918 cm^{-1} and the narrow full width at half maximum (FWHM) of 17 cm^{-1} indicate that the monolayer is crystalline and close packed. In a less crystalline or more disordered monolayer, the position of this band shifts to a higher wavenumber, and the FWHM increases. Sagiv has reported that for a complete monolayer, the intensity of this prominent methylene band increases linearly with the number of methylene groups present in the adsorbed molecule[23]. In the spectrum shown, the intensity of this band

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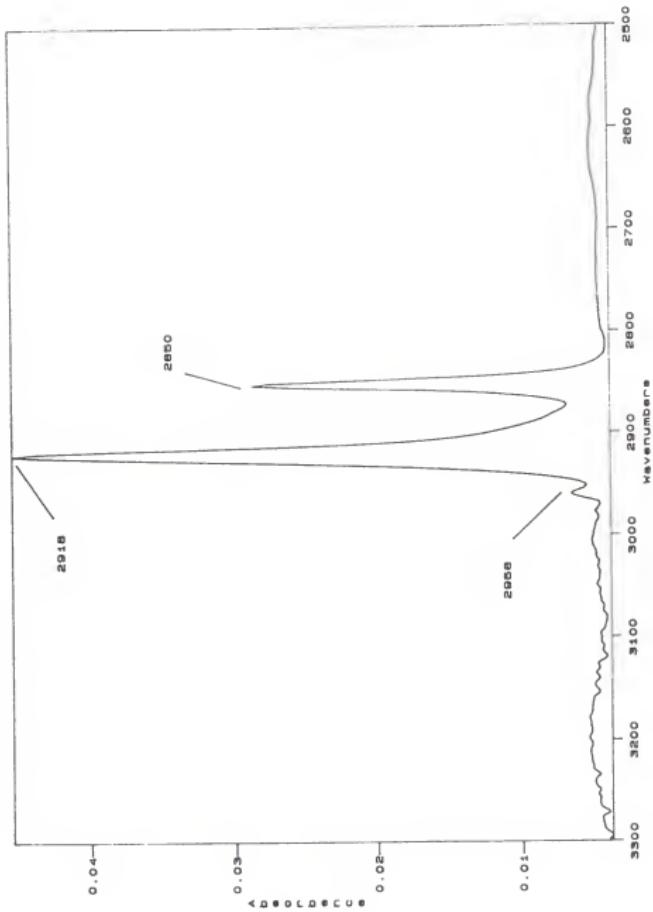
Figure 11 ATR spectrum of $Cl_3Si(CH_2)_7CH_3$

is 0.045 absorbance units (A). Dividing by seventeen gives an approximate absorbance of 2.6×10^{-3} A per methylene unit. The magnitude of absorption observed in this spectrum is consistent with the magnitude of adsorption of monolayer spectra reported in the literature. Although not rigorously quantitative, the intensity of this band can be used as a quick gauge of the amount of surface coverage.

The ATR-FTIR spectrum of the film resulting from the adsorption of $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$ is shown in Figure 12. Although alkyltrichlorosilanes form complete monolayers in a few minutes at room temperature, the substrate had to be immersed in a warm bicyclohexyl solution of the triethoxysilyl phosphonate for at least three days before an intensity of the magnitude anticipated for monolayer coverage, approximately 3×10^{-3} A per methylene unit, was obtained for the most intense methylene band. The hydrolysis of the ethoxy groups necessary for monolayer formation is much slower than the hydrolysis of the chloro groups of trichlorosilanes. The position of the large methylene band at $2926 cm^{-1}$ and the FWHM of $34 cm^{-1}$ indicate that the adsorbed film is very disordered and liquid-like. There are three factors which contribute to the poor quality of this monolayer. First, the eleven carbon chain is probably too short to give a crystalline monolayer; however, this problem is easily corrected by using ω-hexadecenylbromide for the synthesis of the phosphonate instead of using ω-undecenylbromide. More problematic are the ethoxy groups on Si, which are difficult to hydrolyze, and the bulky diethyl phosphonate groups which limit how closely the molecules can pack.
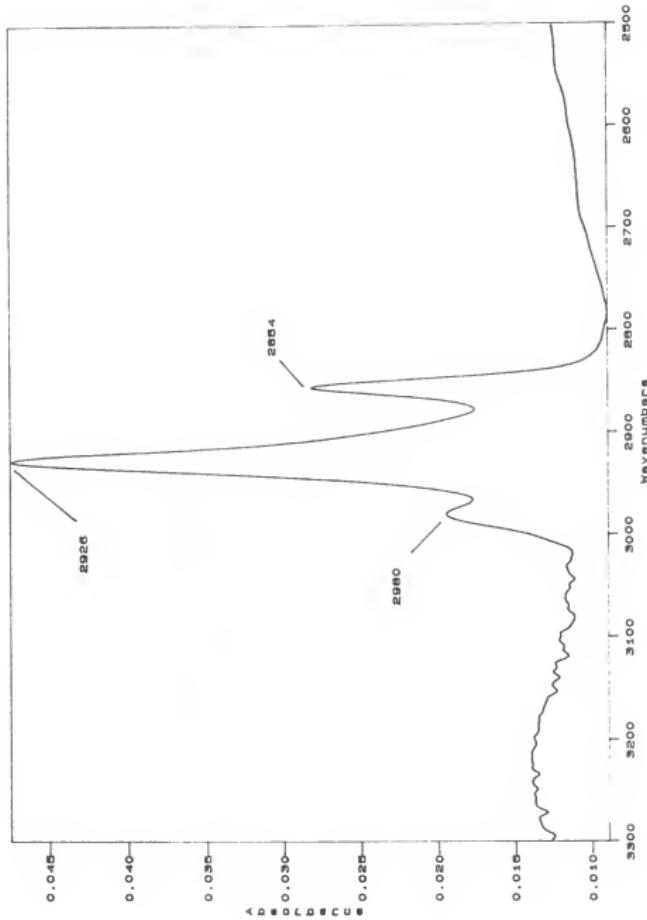
Figure 12   ATR spectrum of $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$

The ATR-FTIR spectrum of a monolayer of $Cl_3Si(CH_2)_{16}Br$ is shown in Figure 13. The spectrum of this bromide terminated monolayer has a methylene band at 2920 cm^{-1} with a FWHM of 25cm^{-1}, and an average absorbance per methylene unit of 2.5×10^{-3} A. Although perhaps not as crystalline as an OTS monolayer, the packing in this film does appear to be superior to that obtained from the assembly of $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$. Extending the chain length from eleven to sixteen carbons and replacing the bulky diethyl phosphonate group by a less bulky bromide functionality favor closer packing in the monolayer. It is not surprising that this molecule does not pack quite as tightly as OTS, which has a slightly longer chain and a small methyl group on the end of the chain.

Figure 14 shows the ATR-FTIR spectrum of the monolayer resulting from the conversion of the surface bromides to diethyl phosphonates. Notable in this spectrum is the appearance of a new band at 2980cm^{-1}. This band is due to the methyl stretch of the ethoxy groups, and is consistent with the position of this band in the spectrum of the triethoxysilyl phosphonate shown previously. In this spectrum, the methylene band which appeared at 2920cm^{-1} in the bromide monolayer has shifted to 2922cm^{-1}. The FWHM has also increased from 25 to 34cm^{-1}. These increases in wavenumber and width indicate that the replacement of the bromide with the bulky diethyl phosphonate group has caused some disorder in the film, however, this film is still more crystalline than the one resulting from the adsorption of $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$. There is a slight decrease in the intensity of the predominant methylene band from 0.04 A in the bromide spectrum to 0.03A in the

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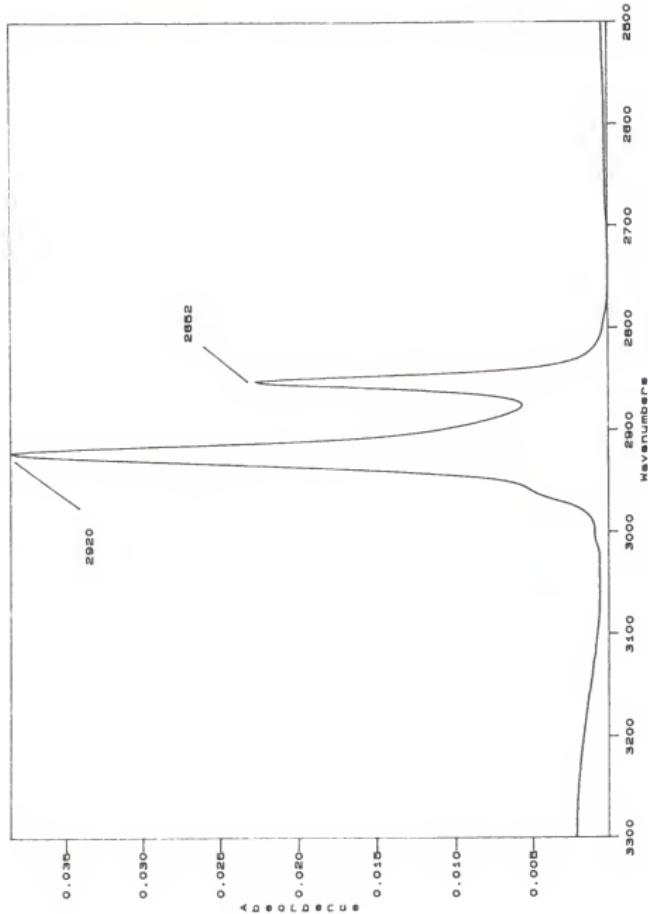
Figure 13   ATR spectrum of Cl$_3$Si(CH$_2$)$_{16}$Br
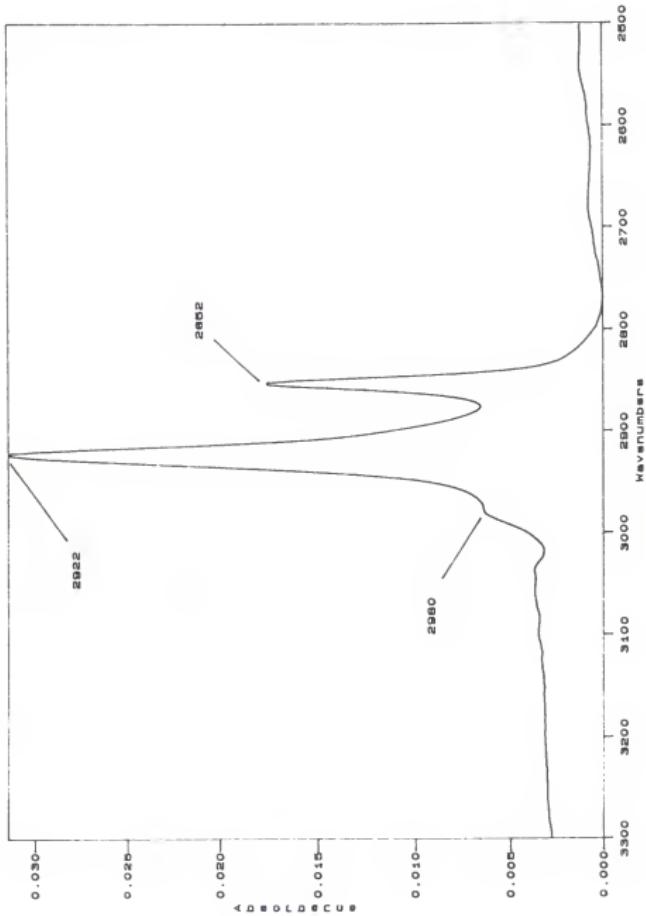
Figure 14 ATR spectrum of -(CH$_2$)$_{16}$P(O)(OEt)$_2$

phosphonate spectrum. This may be an indication that the reaction conditions used for the bromide to phosphonate conversion are causing the desorption of some of the adsorbed monolayer. However, the band width also increases, so a drop in height as the signal spreads out is not unreasonable. More work needs to be done to determine whether or not some of the film is actually being removed.

The diethyl phosphonate monolayer was converted to a phosphonic acid terminated monolayer by acid hydrolysis. The ATR-FTIR spectrum of the film obtained after hydrolysis is shown in Figure 15. The band at 2980cm^{-1} has disappeared, indicating that the ethoxy groups have been cleaved. Unlike alcohols and carboxylic acids, the OH band in the P-OH functional group is a very broad and weak band usually found between 2700-2500 cm^{-1} [43]. Because this band is so broad and weak, it is not seen in the monolayer spectrum. The new band at 2962cm^{-1} can be attributed to the methylene stretch of the methylenes attached to the phosphonic acid group. Polar groups attached to methylenes are known to cause a shift to higher wavenumber[43]. Ulman has observed this type of methylene shift in a monolayer containing an SO_2 group[33]. Figure 16 is a spectrum of $H_2O_3P(CH_2)_{10}PO_3H_2$ in a KBr pellet. It can be seen from this spectrum that the presence of the phosphonic acid groups does indeed cause a splitting of the asymmetric methylene signal.

The ATR-FTIR spectrum shown in Figure 17 was obtained after the phosphonic acid terminated monolayer was zirconated and then capped with octadecylphosphonic acid. Although there is an increase in the intensity of the methylene signal indicating that more organic has been incorporated into the film, the
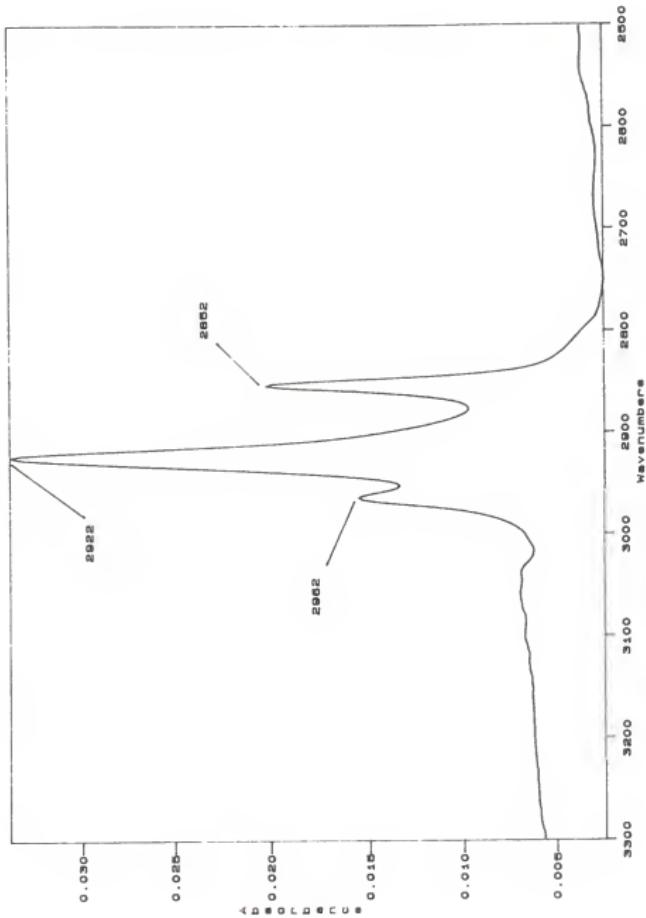
Figure 15 ATR spectrum of -(CH$_2$)$_{16}$PO$_3$H$_2$
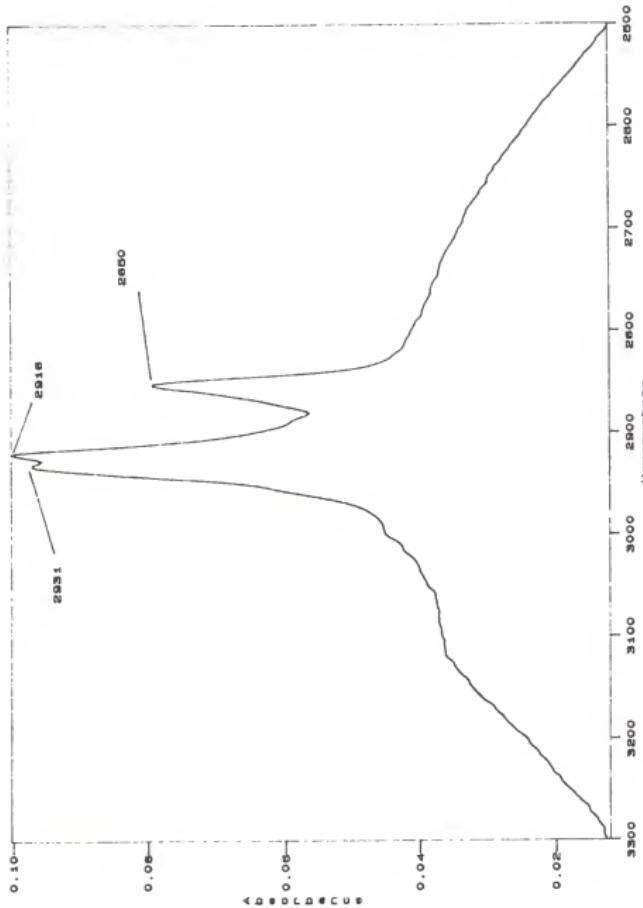
Figure 16   IR spectrum of $H_2O_3P(CH_2)_{10}PO_3H_2$
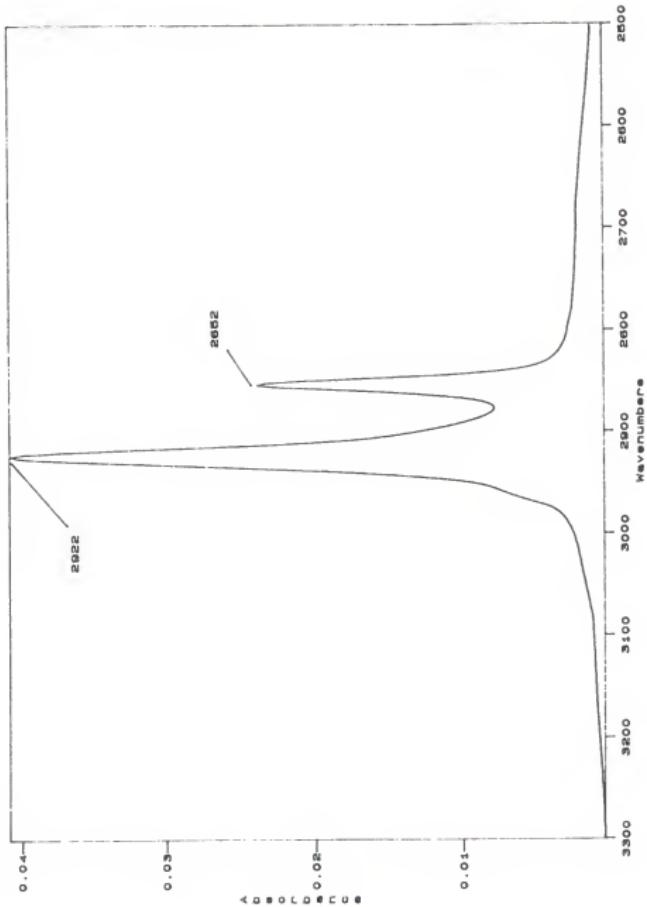
Figure 17   ATR spectrum of zirconated and capped monolayer

intensity increase is not nearly what would be expected if a complete second layer of the capping acid had assembled. More work needs to be done to determine why capping is incomplete.

These monolayer films have also been studied by Electron Spectroscopy for Chemical Analysis (ESCA). Representative ESCA spectra are shown for the bromide monolayer (Figure 18), the phosphonate monolayer (Figure 19), the zirconated acid template (Figure 20), and the capped zirconium layer (Figure 21), respectively. Table 1 lists the binding energies observed for the elements present in each sample. The peaks in the range of 100-200eV which are not included in the table are peaks due to silicon in the substrate and in the anchoring functionality. As expected, bromine is present in the first spectrum. In the spectrum of the phosphonate monolayer, which was prepared from the bromide monolayer by reaction with triethylphosphite, the bromine signal has disappeared and a signal due to phosphorus is now present. Both phosphorous and zirconium are present in both the zirconated film which has not been capped and in the capped sample.

Integration of the peak areas for the P and Zr signals gives information on the relative amounts of these elements present in the film. Table 2 shows the calculated relative concentrations of both Zr and P in two samples after zirconation and after capping. In the bulk zirconium phosphonate structure, the ratio of Zr to P is one to two. Thus, if the monolayer being formed assumes the same packing as the bulk model, a ratio of one Zr to one P is anticipated for the zirconated monolayer before capping, and a ratio of one Zr to two P's is expected after adsorption of the capping

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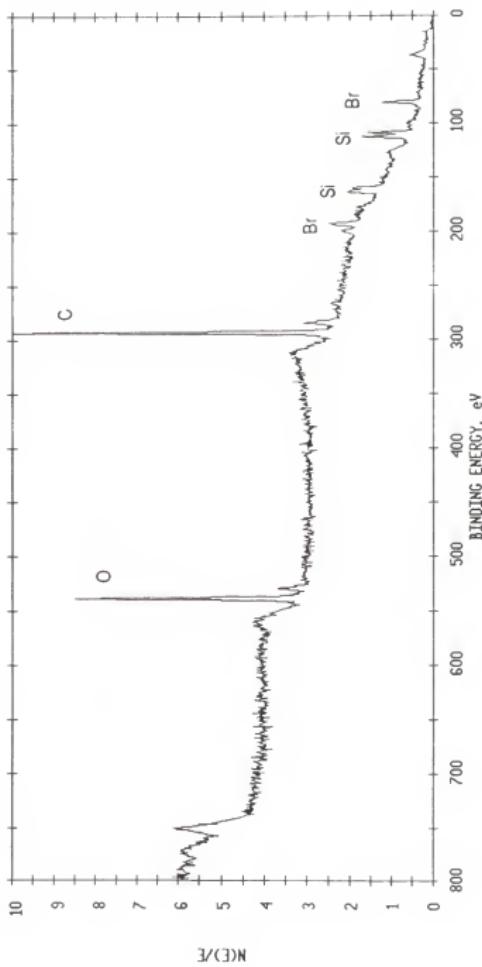
Figure 18   ESCA spectrum for the bromide monolayer

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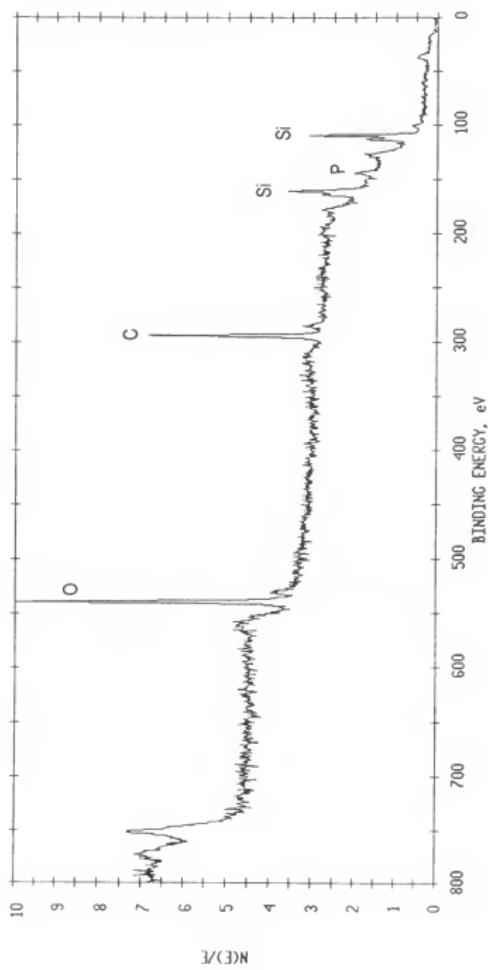
Figure 19   ESCA spectrum of the phosphonate monolayer
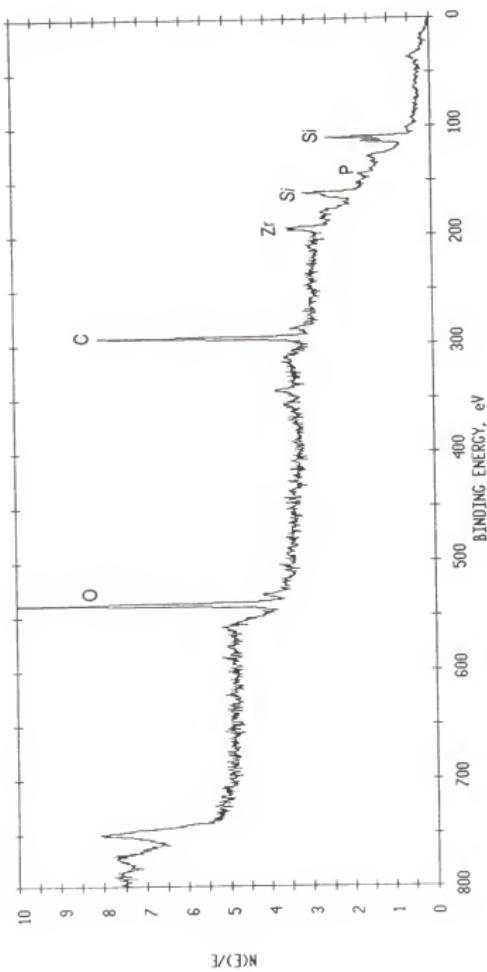
Figure 20   ESCA spectrum of the phosphonic acid template after binding of zirconium
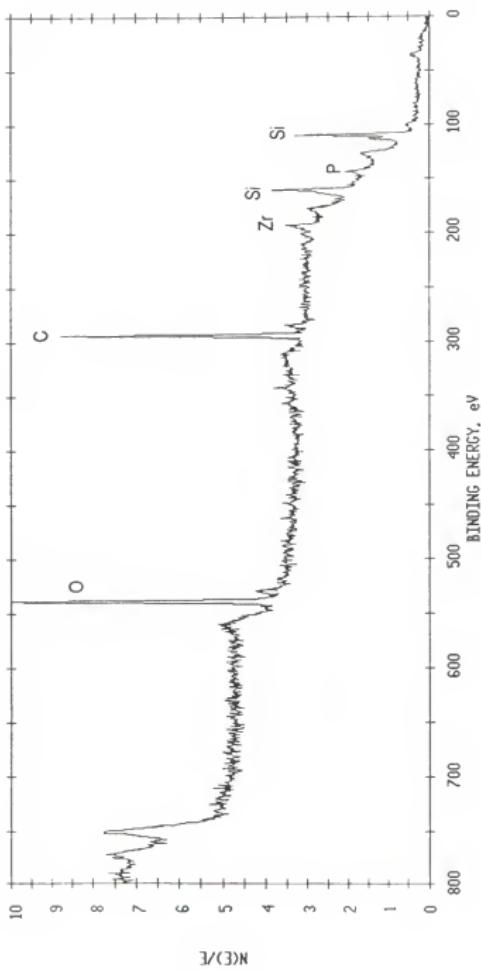
Figure 21   ESCA spectrum of the capped zirconium layer

Table 1   Elemental Composition Determined by ESCA

Sample Type	Binding Energies (eV)					
	Br(3d)	Br(3p)	P(2p)	Zr(3d)	C(1s)	O(1s)
--Br	81	199 193	NP	NP	293	539
--P(O)(OEt)$_2$	NP	NP	143	NP	293	539
--PO$_3$-Zr	NP	NP	143	192.5 195	293	539
--PO$_3$-Zr-O$_3$P--	NP	NP	143	192.5 195	293	539

*NP indicates that the element was not present in the ESCA spectrum.

Table 2   Relative Amounts of Zr and P Determined by ESCA

	%P	%Zr	ratio (P:Zr)
uncapped-1	53.95	46.05	1:1
uncapped-2	64.49	35.51	2:1
capped-1	76.26	23.74	3:1
capped-2	76.08	23.92	3:1

organic layer. Before capping, Zr and P are present in the anticipated ratio of one to one in the first sample, but are present in a ratio of one to two in the second. After capping, the ratio of Zr to P is approximately one to three for both samples, instead of the ratio of one to two found in bulk zirconium phosphonates. Although at least some Zr and some capping acid are being incorporated into the monolayer assembly, it is clear that the experimental conditions currently being employed do not allow formation of a complete monolayer analog of bulk Zr phosphonates.

Attempts to bind manganese ions from aqueous solution to a phosphonic acid terminated SA monolayer were unsuccessful. Manganese was not detected by ESCA on a phosphorylated sample which had been treated with the manganese chloride solution. In addition, ATR-FTIR shows no increase in the intensity of the methylene signals after the substrate was dipped in the manganese solution, followed by the capping acid solution. Presumably, no capping acid could be bound to the phosphorylated substrate because no metal ions were present as binding sites.

CONCLUSIONS

Synthesis of a monolayer analog of a layered magnetic solid will allow the study of magnetic behavior in two dimensions. Manganese phenylphosphonate, $Mn(O_3PC_6H_5)H_2O$, undergoes a transition to long range antiferromagnetic order at low temperature. This layered solid has been chosen as a model compound of which synthesis of a two dimensional analog will be attempted.

One approach to the synthesis of an inorganic monolayer analog of metal phosphonates is to utilize an appropriately functionalized organic SA monolayer as a template for binding the inorganic layer. Such a template could be prepared by the adsorption of a silane containing a terminal phosphonic acid group onto a hydroxylated surface, such as SiO_2. Several synthetic routes to a phosphonic acid terminated organic SA monolayer have been investigated.

The first route investigated involves the synthesis of $Cl_3Si(CH_2)_{11}P(O)(OEt)_2$. This silane could then be assembled into a monolayer film and the diethyl phosphonate functionality hydrolyzed to a phosphonic acid. Attempts to prepare the necessary trichlorosilyl phosphonate have been unsuccessful, resulting in the formation of a polymer product.

Since $Cl_3Si(CH_2)_{11}P(O)(OEt)_2$ could not be synthesized, synthesis of the corresponding triethoxysilane, $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$, was attempted. This silane

has been synthesized, but only with great difficulty. It appears that the presence of the phosphonate functional group poisons the chloroplatinic acid catalyst used for the addition of triethoyxsilane across the double bond in the synthesis of this molecule.

In addition to the difficult synthesis of $(EtO)_3Si(CH_2)_{11}P(O)(OEt)_2$, using this silane to form an ordered SA monolayer suitable for use as a template was also problematic. The mechanism for adsorption of silane monolayers involves first hydrolyzing the halogen or alkoxy groups on silicon, followed by condensation of the resulting silanols with the hydroxylated substrate. Because ethoxy groups are much more difficult to hydrolyze than chloro groups, adsorption of this silane proceeds exceedingly slowly. Also, the presence of the bulky phosphonate group in this silane may prevent close packing of the adsorbing molecules.

Because of the problems encountered in attempting to prepare monolayers of a silane containing a phosphonate group, it was decided that perhaps a better approach to a phosphonic acid terminated template would be to prepare a SA monolayer containing a functional group which could be converted to the desired phosphonic acid functionality after the monolayer was formed. To investigate the feasibility of such an approach, an SA monolayer containing a terminal bromide functionality was synthesized. The monolayer film was then reacted with triethylphosphite to convert the surface bromides to diethyl phosphonates, followed by acid hydrolysis to the desired phosphonic acid functionalities. Conversion of the surface bromides to phosphonic acid groups does appear to be a viable route to a phosphorylated template; however, there is evidence which suggests that some material may be lost from the

film during the reaction of the bromide monolayer with triethylphosphite. More work needs to be done to determine whether or not some of the film is actually being removed from the substrate.

To evaluate the usefulness of the phosphonic acid film prepared from the bromide monolayer as a template for the synthesis of metal phosphonate monolayers, the phosphorylated substrate was treated with solutions of zirconyl chloride and a capping phosphonic acid. Although analysis by ESCA and ATR-FTIR indicate that some zirconium and some capping acid are being bound to the template, it appears that a complete zirconium phosphonate monolayer analogous to a layer in the bulk solid is not being formed. Further investigation is necessary to develop conditions which do promote the formation of a complete inorganic monolayer. One concern which should be investigated is that the packing of the phosphonic acid groups in this template may not be suitable for binding a complete monolayer of the inorganic system.

The binding of divalent manganese to the phosphonic acid template has also been attempted, but without success. It is not surprising that manganese does not bind to the phosphonic acid groups as readily as zirconium, since bulk manganese alkylphosphonates are generally more soluble than bulk zirconium alkylphosphonates. In future attempts to synthesize manganese phosphonate monolayers, perhaps a manganese complex with easily replaced ligands could be used as a source of manganese. Also, varying the solvent used for preparation of the dipping solution may allow manganese to be incorporated at the organic template.

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BIOGRAPHICAL SKETCH

Margaret Leigh Crews was born on January 25, 1967 in Prince Edward County, Virginia. Her parents are Richard Samuel and Virginia Bernard Crews of Meherrin, Virginia. She attended Lunenburg County Public Schools and was graduated from Central Senior High School in 1985, where she was valedictorian of her class. In August of 1985, she enrolled at Mary Washinton College in Fredericksburg, Virginia. At Mary Washinton, Ms. Crews was named a Regional Scholar and was inducted into Phi Beta Kappa. She graduated magna cum laude in May of 1989 with a B.S. in chemistry. That fall, she enrolled in the graduate program in the Department of Chemistry at the University of Florida, Gainesville, Florida. Her area of specialization was inorganic chemistry, and her research was directed by Dr. Daniel R. Talham. She received a M.S. from the University of Florida in 1992. On May 16, 1992, she married Steven K. Showalter. She now goes by the legal name of Margaret Crews Showalter.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

Daniel R. Talham, Chairman
Assistant Professor of Chemistry

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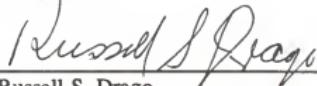
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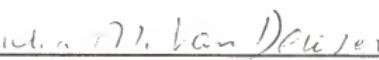
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This thesis was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Master of Science.

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Dean, Graduate School